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Accessing the Single Electron Manifold: Magnesium-mediated Hydrogen Release from Silanes

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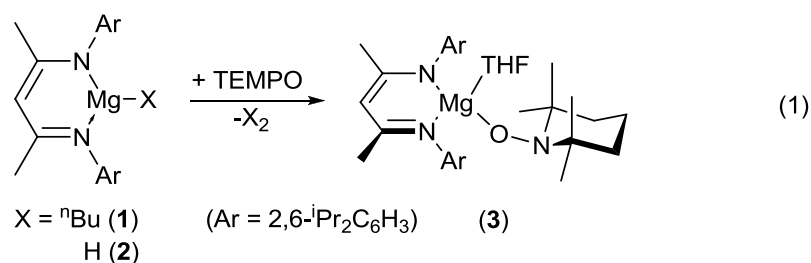
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Reactions of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) with magnesium hydride species initiate oxidative hydrogen release, which may be elaborated to a catalytic regime within a manifold constructed about sequential TEMPO-mediated redox and Mg-O/Si-H metathesis processes.

The stable nitroxyl radical, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), has attracted widespread interest since its first synthesis in 1959.^[1] Much of this attention has centered on its utility in polymer synthesis,^[2] organic oxidation reactions^[3] and, due to its persistent radical character, in molecular magnetism.^[4] Although the use of TEMPO as a radical donor ligand is dominated by reports of redox-active *d*-block complexes,^[5] there is also more limited precedent for the use of TEMPO in *d*⁰ *f*-^[6] and *s*-block^[7] complex chemistry. Mulvey and co-workers reported the first group 1 and 2 complexes of TEMPO in 2001,^[7a] noting not only its coordination as a neutral two electron donor but also its ability to adopt an anionic electron configuration when ligating group 2 cations in complexes of the form [$\{(\text{Me}_3\text{Si})\text{N}\}\text{Mg}\{\mu\text{-TEMPO}\}\text{Mg}\{\mu\text{-TEMPO}\}\text{N}(\text{Me}_3\text{Si})\text{N}\}]_2$. A subsequent, elegant report from this group of single electron transfer (SET) from elemental group 1 metals to TEMPO yielded a structurally diverse series of $[\text{M}\{\text{TEMPO}\}]$ compounds ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) once again containing TEMPO anions (hereafter referred to as TEMPOxide).^[7b] A demonstration of TEMPO reactivity with group 2 reagents has also been described by Fedushkin *et al* who reported SET with a magnesium complex mediated by a redox-active 1,2-bis(arylimino)acenaphthene (BIAN) ligand.^[7d] Furthermore, stoichiometric SET to organomagnesium reagents is well precedented, yielding a variety of C-C and C-N coupled products.^[8] Although this reactivity has not yet been extended to magnesium hydride species, it is notable that Jones *et al* have reported that stoichiometric reactions of TEMPO with a range of group 13 hydrides yield molecular dihydrogen alongside the formation of TEMPOxide ligated to the relevant group 13 center.^[9]

There is growing awareness of the ability of heavier alkaline earth reagents (Mg, Ca, Sr, Ba) to engage in a plethora of heterofunctionalization and bond-forming catalyses.^[10] While reductive processes, based on group 2 hydride intermediates generated by metathesis of silane and borane reagents at amide- and alkoxide-ligated centers, have been central to recent progress,^[11] a severe limitation to further development is a restriction to catalytic manifolds derived solely from two electron bond breaking/forming processes. Herein, we report the activity of TEMPO towards magnesium hydrides and the utility of subsequent silane metathesis for the development of oxidative hydrogen release catalysis. This is, to the best of our knowledge, the first report of redox-based catalysis by an *s*-block metal complex and establishes the viability of SET reactivity in the catalytic applications of the benign and inexpensive alkaline earth elements.

Our initial investigations centered upon magnesium β -diketiminate complexes, $[\text{CH}\{\text{C}(\text{Me})\text{NAr}\}_2]\text{Mg}^n\text{Bu}$ (**1**)^[12] and $[\text{CH}\{\text{C}(\text{Me})\text{NAr}\}_2]\text{MgH}_2$ (**2**)^[13] (Ar = 2,6-*i*PrC₆H₃). Gratifyingly, the action of TEMPO upon both these species evidenced SET characteristics with almost instantaneous extinction of the red colour associated with TEMPO. Monitoring by ¹H NMR spectroscopy revealed that compound **1** had undergone a well-precedented alkyl coupling to form *n*-octane,^[7c] while compound **2**, in reactivity reminiscent of that reported for group 13 hydrides,^[9] provided a pronounced bubbling of molecular dihydrogen (eqn. 1). Alongside the desired small molecule products of this reaction, a magnesium complex (**3**) was isolated and characterized by NMR spectroscopy and single crystal X-ray diffraction analysis (Figure 1).



Although the coordination environment of compound **3** is otherwise comparable to Fedushkin's BIAN derivative, wherein the nitroxide nitrogen center displays significant pyramidalization indicative of single electron reduction of the

radical starting material,^[7d] the two compounds differ significantly in the mode of binding of the TEMPO_x ligand. Whereas the TEMPO_x binds in an unambiguous η^1 coordination mode through the terminal oxygen center in **3**, coordination to the BIAN-coordinated magnesium occurs through both the nitroxide oxygen and nitrogen centers. Although the causes of the structural change are unclear, this adjustment results in a significant shortening of the Mg-O distance within compound **3** [1.8887(13) *versus* 1.9061(10) Å]

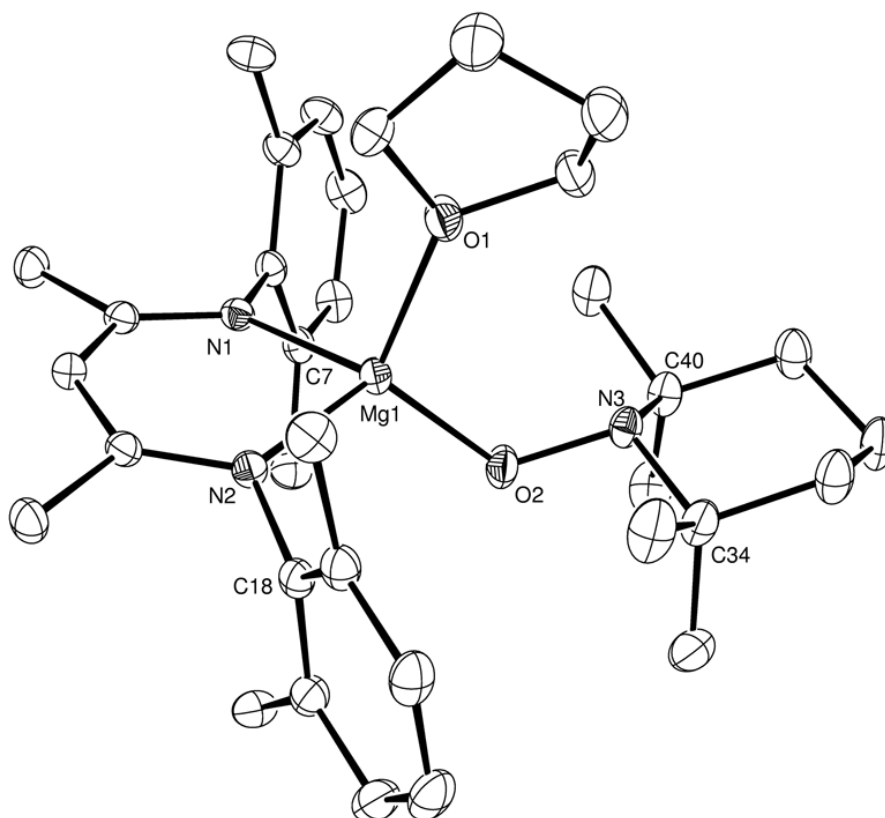
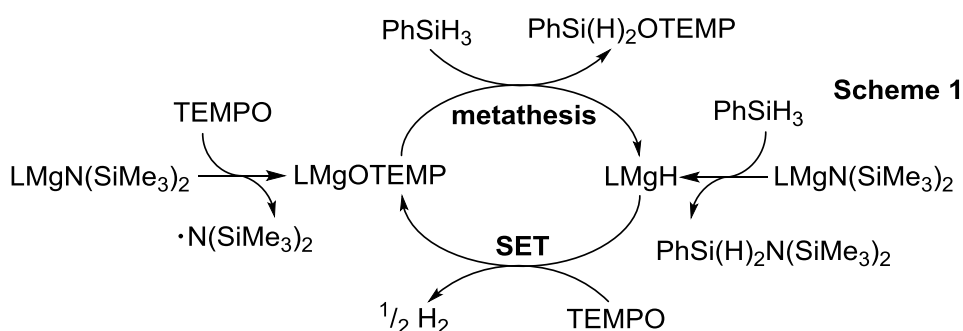


Figure 1: ORTEP representation of **3** (30% probability ellipsoids). *Iso*-propyl methyl groups and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-O2 1.8887(13), Mg1-O1 2.0534(14), Mg1-N2 2.0844(14), Mg1-N1 2.0915(15), O(2)-N(3) 1.4423(1), O2-Mg1-O1 111.07(6), O2-Mg1-N2 117.99(6), O1-Mg1-N2 108.31(6), O2-Mg1-N1 119.43(6), O1-Mg1-N1 105.45(6), N2-Mg1-N1 92.65(6), O2-N3-C40 108.71(13), O2-N3-C34 108.82(13).

Attempts to extend this reactivity to a catalytic manifold, reliant upon the conversion **3** into **2** via σ -bond metathesis, were undertaken utilizing phenylsilane as a hydride source. Unfortunately no reactivity between **3** and PhSiH₃ was observed

which we attribute to the steric demands of the various substituents surrounding the magnesium center precluding approach of the silane reagent. Consequently, our attention turned to the less sterically congested homoleptic magnesium amide and alkyl pre-catalysts, $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ (**4**) and Bu_2Mg (**5**). While TEMPO and PhSiH_3 displayed no background reactivity in the absence of the magnesium reagents, reactions in the presence of 10 mol% **4** or **5** in C_6D_6 induced an observable bubbling and the decolorization of the solution over the course of days. Analysis of the resultant solution by NMR spectroscopy also confirmed the formation of a new silane containing species, proposed to be $\text{TEMPOSi}(\text{H})_2\text{Ph}$, formed via a catalytic manifold reliant upon both SET and σ -bond metathesis (Scheme 1). The reaction was optimized with respect to a small range of solvents, with the donor solvent d_8 -THF providing significantly enhanced reaction rates in comparison to the aromatic solvents investigated, C_6D_6 and d_8 -toluene.



A series of stoichiometric investigations were undertaken to elucidate the intermediate species participating in this reaction. Reaction of **5** with two equivalents of TEMPO in THF yielded stepwise activation of the magnesium-bound butyl groups giving rise to a crystallographically characterized heteroleptic TEMPOxide-alkyl $[(\text{THF})\text{Mg}(\text{TEMPO})(\text{Bu})_2]$ (**6**) (see Figure S1) and the anticipated homoleptic magnesium TEMPOxide complex, $[(\text{THF})\text{Mg}(\text{TEMPO})_2]_2$ (**7**), which was isolated and characterized by NMR spectroscopy and a further single crystal X-ray diffraction analysis (Figure 2). The dimeric structure of compound **7** comprises terminal and bridging TEMPOxide ligands. Most notably, the bridging Mg-O interactions within the structure of **7** [1.9869(11), 1.9891(1) Å] are similar to those of Mulvey's structurally related complex, $[\{(\text{Me}_3\text{Si})\text{N}\}\text{Mg}\{\mu\text{-TEMPO}\}]_2$,^[7a] but are significantly elongated in comparison to both the terminal distances within the dimeric unit itself

[1.8848(11) Å] and the unique TEMPOxide ligand of compound **3**. Although monitoring of reactions of isolated samples of **7** with an excess of phenylsilane by ^1H NMR spectroscopy evidenced the formation of the proposed silane containing product, $\text{TEMPOSi(H)}_2\text{Ph}$, the magnesium hydride intermediate implicated in the proposed mechanism was not observed. Rather, under these stoichiometric conditions an intractable colorless solid, proposed to be bulk magnesium hydride, was observed to precipitate from THF solution.

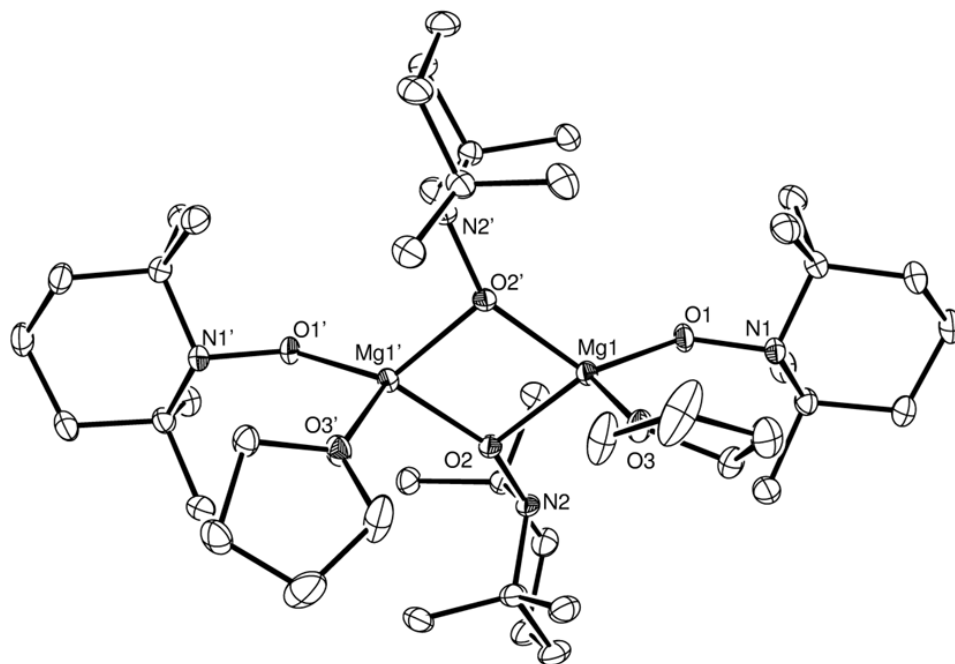


Figure 2: ORTEP representation of **7** (30% probability ellipsoids). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-O1 1.8848(11), Mg1-O2 1.9869(11), Mg1-O2' 1.9891(1), Mg1-O3 2.0763(12), O1-N1 1.4420(15), O2-N2 1.4551(15), O1-Mg1-O2 126.70(5), O1-Mg1-O2' 127.26(5), O2-Mg1-O2' 79.54(5), O1-Mg1-O3 104.77(5), O2-Mg1-O3 110.22(5), O2'-Mg1-O3 105.78(5), N1-O1-Mg1 130.91(9), N2-O2-Mg1 106.85(8), N2-O2-Mg1' 150.75(8), Mg1-O2-Mg1' 100.20(5). Symmetry transformations used to generate equivalent atoms: (') - $x, y, -z+1/2$.

Table 1: The results of the scope study into silane (0.1 mmol) coupling partners with TEMPO mediated by $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ (**4**) (0.01 mmol) in 4:1 THF: C_6D_6 (0.5 mL).

Entry	Silane	Silane:TEMPO ratio	Product	Time (d)	Temp. (°C)	Conv. (%)
1	PhSiH ₃	1:1	PhSi(H) ₂ OTEMP	1	60	99
2		1:2	PhSi(H)OTEMP ₂	6	80	96
3	Ph ₂ SiH ₂	1:1	Ph ₂ Si(H)OTEMP	3	60	97
4		1:2	Ph ₂ Si(H)OTEMP	4	80	99
5	Ph(Me)SiH ₂	1:1	Ph(Me)Si(H)OTEMP	1	80	77
6	Et ₃ SiH	1:1	N/A	3	80	0
7	Ph ₃ SiH	1:1	N/A	3	80	0

The influence of substitution on the silane coupling partner for reactions catalyzed by compound **4** was investigated through an evaluation of the reaction scope (Table 1). Although limited, this study allowed the delineation of several trends, most notably a significant dependence on substrate bulk. The least hindered primary silane (entry 1) was found to react far more rapidly than secondary silanes (entries 2, 3 and 5) while tertiary silanes were too sterically encumbered to engage in onward reaction with the magnesium TEMPOxide, even at elevated temperatures and extended reaction times (entries 4, 6 and 7). These data are consistent with limitations previously observed for the magnesium-mediated coupling of amines with silanes.^[11g] Further TEMPO substitution of the silane substrate was also only possible for the least sterically congested silane coupling partner, PhSiH₃ (entry 2).

Further mechanistic insight into this reaction was provided by a preliminary kinetic study performed by ¹H NMR analysis of the reaction between PhSiH₃ and TEMPO mediated by **4**. After an initial induction period, which we attribute to the slow formation of an intermediate magnesium TEMPOxide species structurally related to **7**, the reaction was found to be well described by second-order kinetics (Figure S2). The formation of this species coincided with the generation of HN(SiMe₃)₂, which is cautiously attributed to the coupling of hexamethydisilazyl and hydrogen radical species. A *pseudo*-first order study (Figure S3) with a tenfold excess

of phenylsilane, however, indicated a first-order dependence on [TEMPO] and a rate determining process predicated upon the presence of one equivalent of phenylsilane and one equivalent of TEMPO at the catalytic reaction center. We tentatively interpret this latter deduction as suggestive of a rate determining step in which one molecule of silane is transformed to the silyl TEMPOxide and one molecule of TEMPO facilitates the assembly of the requisite polarized transition states in a manner broadly reminiscent of ‘frustrated’ Lewis pair behavior^[14] and the proton-assisted pathways integral to successful turnover of group 2-centered olefin hydroamination catalysis.^[15] Further studies to more fully elucidate the nature of the rate determining process are ongoing.

In summary, we have described the first example of SET reactivity which is catalytic in an *s*-block metal. This oxidative coupling is mediated by a magnesium(II) center and yields dihydrogen and a series of TEMPO silylethers. Catalytic turnover most likely proceeds *via* a catalytically active magnesium TEMPOxide which engages in Si-H/Mg-O σ -bond metathesis to yield an intermediate magnesium hydride species and the silylether. The action of TEMPO upon this magnesium hydride proceeds by SET and, to the best of our knowledge, constitutes the first example of the action of TEMPO on a group 2 hydride. We are continuing to explore this reactivity and to elaborate further group 2-centered protocols which couple σ -bond metathesis to SET steps for productive bond-forming catalysis.

Methods

Details of the synthesis, characterization data and the crystallographic protocols employed in this study are given in the Supporting Information. CCDC 990851 - 990853 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.ca.ac.uk/data_request/cif.

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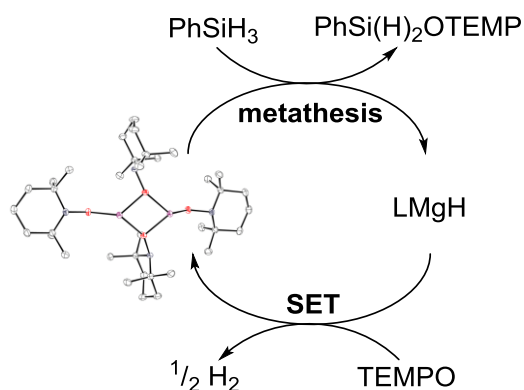
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Accessing the Single Electron Manifold: Magnesium-mediated Hydrogen Release from Silanes

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Upping the tempo: Reactions of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) with magnesium hydride species initiate catalytic hydrogen release through sequential TEMPO-mediated redox and Mg-O/Si-H metathesis processes.



Keyword: Magnesium, Catalysis, Single-electron, Metathesis, TEMPO